Synthesis of Single Phase $SrCu_2O_2$ From Liquid Precursors

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August 15, 2002

Prepared in partial fulfillment of the requirements of the Office of Science, DOE Energy Research Undergraduate Laboratory Fellowship under the direction of David Ginley in the National Center for Photovoltaics at the National Renewable Energy Laboratory.

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Abstract

Synthesis of Single Phase $SrCu_2O_2$ From Liquid Precursors. ALEX MARTINSON (Luther College, Decorah, IA, 52101) D.S. GINLEY (National Renewable Energy Laboratory, Golden, CO, 80401).

We report on the first successful non-vacuum deposition of single phase $SrCu_2O_2$ from liquid precursors by spray deposition as well as experiments on the deposition of $SrCu_2O_2$ thin films by inkjet printing. Liquid precursors for $SrCu_2O_2$ were made by dissolving copper formate and strontium acetate in water. Bulk single-phase powdered $SrCu_2O_2$ was synthesized through the spray deposition of liquid precursors at 180°C followed by a 4 hour anneal at 775°C and 2.0 x 10^{-5} Torr vacuum. Additionally, $CaCO_3$ was successfully added to the precursor solution above and subsequently incorporated after annealing. This was a critical demonstration of the ability to do cation substitutions by this approach. Employing the liquid precursor for thin films resulted in mixed phase $SrCu_2O_2$ and Cu_2O due to Sr loss during annealing. The liquid precursor was also successfully inkjet printed.

Research Category: Materials Sciences

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Is this being submitted for publication? Yes - Edited
DOE Program: ERULF

Introduction

Transparent conducting oxides (TCOs) are widely used in solar cells, flat panel displays, electrochromic windows, and various other opto-electronic devices.[1] While many n-type TCOs are known and currently in use, TCOs that exhibit p-type conduction are still rare. Recently, several d^{10} copper oxides, including $SrCu_2O_2$, CuAlO2, $CuGaO_2$ have demonstrated p-type conductivity.[2-4] $SrCu_2O_2$ is of particular interest because recent studies have shown it to have wide band gap and relatively low deposition temperatures.[5] This has tremendous potential for next generation high performance PV as a contact to p-type semiconductors and as a component in a tunnel juntion.[6] In addition, a working transparent diode composed completely of TCOs has now also been fabricated.[7] This transparent diode, the only one of its kind, is composed of p-$SrCu_2O_2$ and n-ZnO. To our knowledge, the reported synthesis of $SrCu_2O_2$ has been through conventional ceramic processing followed by vacuum based pulsed laser deposition to create thin films. In this work we report on a new method of synthesis that is both more economical, potentially environmentally friendly and more conducive to rapid exploration of process and compositional phase space. We report the non-vacuum synthesis of $SrCu_2O_2$ from liquid precursors. The precursors are synthesized inexpensively and are amenable to ready compositional substitution. The liquid precursor approach was chosen with the intention that they could readily be incorporated into inkjet printing in the future. Inkjet printing allows for control of the deposition space as well as a relatively inexpensive method of deposition. Multiple inkjet heads printing may allow for elemental substitution gradients similar to how color inkjet printers can create a gradient of colors.

The first step toward inkjet printing of thin film $SrCu_2O_2$ is the synthesis of the correct phase using the non-vacuum processing and the liquid precursors. We report the synthesis and substitution of bulk phase $SrCu_2O_2$ through spray deposition of liquid precursors. Spin casting allows similar precursors to be spun into thin films. The viability of inkjet printing liquid precursors has also been explored.

Materials and Methods

Liquid precursors to $SrCu_2O_2$ were made by dissolving organometallic powders into liquid solvents. Stoiciometrically correct 1M solutions were prepared by dissolving $Cu(OOCH)_2 \bullet 4H_2O$ and $Sr(CH_3CO_2)_2$ into water. In some samples, $CaCO_3$ were substituted for the $Sr(CH_3CO)_2$ by 10% (atomic ratio).

As an initial test of the ink formulations, bulk powder samples were made by spray deposition. A fused-silica substrate was mounted on a resistive heater positioned 30° from horizontal and heated to 180°C. The precursor solution was passed through a 0.2 μm syringe filter and sprayed with an artist's airbrush. Approximately 3 ml of solution was deposited over 5 minutes yielding a thin brown powder. The fused-silica substrates were then secured to a resistive heating element with silver paste and sealed in a vacuum chamber with a base pressure 2.0×10^{-6} Torr. The samples were annealed in vacuum with a controlled oxygen partial pressure to bring the total chamber pressure to 2.0×10^{-5} Torr. After 4 hours of heating at 775°C, the temperature was quickly dropped to 650°C and the oxygen bleed was eliminated before allowing the sample to cool to room temperature.

Multiple liquid precursors in various solvents were successfully spin cast onto fused silica substrates. 4 cm^2 substrates were mounted onto a spin caster (photoresist spinner, Headway Research Inc.). Liquid precursor was filtered through a 0.2 μm syringe filter and 2 drops were deposited onto the substrate. Samples were spun at 2000 rpm for 30 seconds at room temperature. The samples were warmed to 100°C for 30 minutes and then heated to 400°C for 30 minutes. In some cases, multiple layers were deposited by repeating the same process. The same annealing conditions are used as for the spayed case above.

Several liquid precursors in multiple solvents were also inkjet printed onto fused-silica substrates. A 50 micron inkjet print head (50 μm MicroJet™, MicroFab Technologies Inc.) was used to print the liquid precursors.

Samples were characterized using X-ray diffraction (XRD, Scintag Model X1, Cu Kα) and inductively coupled plasma emission spectroscopy (ICP, Varian Liberty 150).

Results and Discussion

Figure 1 shows the XRD θ/2θ pattern for a spray deposited sample annealed at 775°C under argon flow. The resulting mixed phase sample is primarily $SrCuO_2$ and CuO. The development of this phase distribution can be understood by examining the phase space for the (Sr-Cu-O) system, shown as Fig. 2. This phase diagram, based on the work of Suzuki *et al.*[8], shows the various Sr-Cu-O phase fields as a function of oxygen

pressure and temperature for a fixed metals ratio of Cu/Sr = 2 as is appropriate for $SrCu_2O_2$. Taken together, this phase diagram and the XRD results from Fig. 1, suggest that to reach the correct phase, the O_2 partial pressure needed to be decreased. Accordingly, new samples were annealed in a vacuum chamber with a controlled oxygen pressure. The XRD pattern for samples annealed at 775 °C in 2.0 x 10^{-5} Torr O_2 is shown Fig. 3. Pattern a) is the water based precursor spray deposited on fused silica at 180°C after annealing. The liquid precursor resulting in pattern b) substituted $CaCO_3$ for 10 atomic % of the Sr and was annealed under the same conditions. Both samples appear to be highly crystalline and phase pure. Table 1 shows the composition of each sample as determined by ICP. It is clear that the Ca source added to the liquid precursor has survived the annealing process.

The spin cast films were similarly characterized. Figure 4 shows the XRD θ/2θ pattern for a spin cast sample. The precursor is a 0.5M solution of copper formate and strontium acetate in a 70:30 mix of water and 2-propanol. This spectra is taken from a film deposited by spinning 2 layers of 0.5M precursor. The sample is less pure and less crystalline than the spray deposited counterparts. Note the presence of Cu_2O in addition to $SrCu_2O_2$. This suggests that after annealing, the thin film samples are Sr deficient. The ICP results given in Table 2 show further evidence of the incorrect stoichiometry after annealing of several thin film samples. The loss of Sr from the precursor during anneal was unexpected and demonstrates a potential problem for the thin film samples. Additional Sr may be need to be added to the precursor or Sr vapor pressure may need to be controlled during anneal.

The viability of inkjet printing of the liquid precursors was also been explored. The water based precursor could be consistently printed under conditions given in Table 3.

The aim of this work was to provide an alternative synthesis technique for $SrCu_2O_2$ that would be easily and affordably implemented. To our knowledge, this is the first report of synthesis of $SrCu_2O_2$ through liquid precursors. One main advantage of this method of deposition is its potential to explore compositional phase space in the $SrCu_2O_2$ system. Future work includes the optimization of spin cast deposition synthesis as well as inkjet printing of thin film $SrCu_2O_2$ precursors.

Conclusion

We have demonstrated the synthesis of phase-pure bulk $SrCu_2O_2$ through the use of liquid precursors for the first time. Ca has been substituted through the use a liquid precursor and been shown to endure the annealing process. Spin cast thin films have been created using water based liquid precursors. Annealing of the thin films results in a mixed phase of $SrCu_2O_2$ and CuO. The ability to inkjet print the precursors to $SrCu_2O_2$ has also been demonstrated.

Acknowledgments

This work was supported by the National Renewable Energy Laboratory and Department of Energy. Special thanks to David Ginley, Tanya Kaydanova, Alex

Miedaner, and John Perkins for all their assistance that made this work a productive and rewarding experience.

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Figure Captions

Fig. 1: XRD θ/2θ spectra for bulk phase $SrCuO_2$. Liquid precursor spray deposited on fused silica substrate and annealed at 775°C under argon flow for 20 hours. Bottom panel: expected powder pattern intensities (JCPDS 38-1179),

Fig. 2: Sr-Cu-O phase space for Cu/Sr = 2

Fig. 3: XRD θ/2θ spectra of bulk phase (a) $SrCu_2O_2$ and (b) Ca substituted $SrCu_2O_2$. Samples annealed at 775°C and 2.0 x 10^{-5} Torr for 4 hours. Bottom panel: expected powder pattern intensities (JCPDS 38-1178).

Table 1: Ratio of elements in precursors are calculated according to preparation of liquid precursor. Ratio of elements in annealed powders are measurer by ICP emission spectroscopy.

Table 2: Thin film annealed samples showing Sr deficinacy

Table 3: Stable inkjet printer conditions with water based liquid precursor

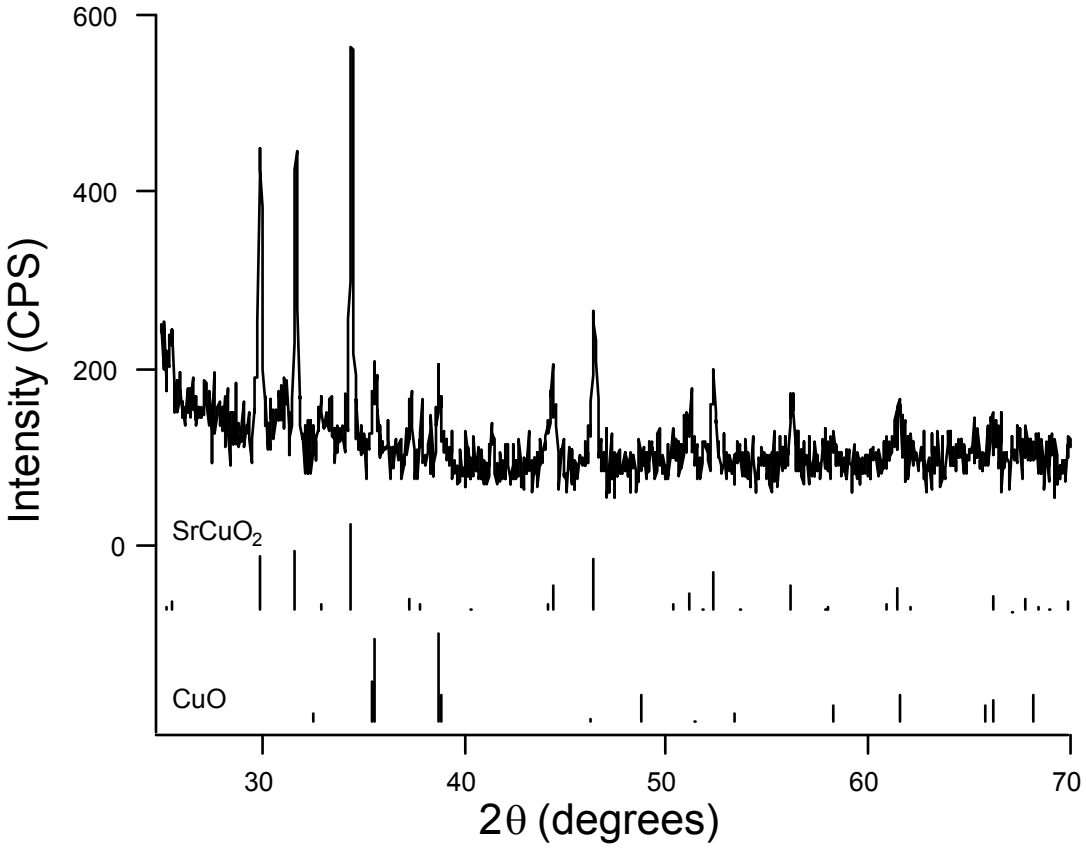
600
400
200
0
Intensity (CPS)
SrCuO2
CuO
30
40
50
60
70
2θ (degrees)

Figure 1

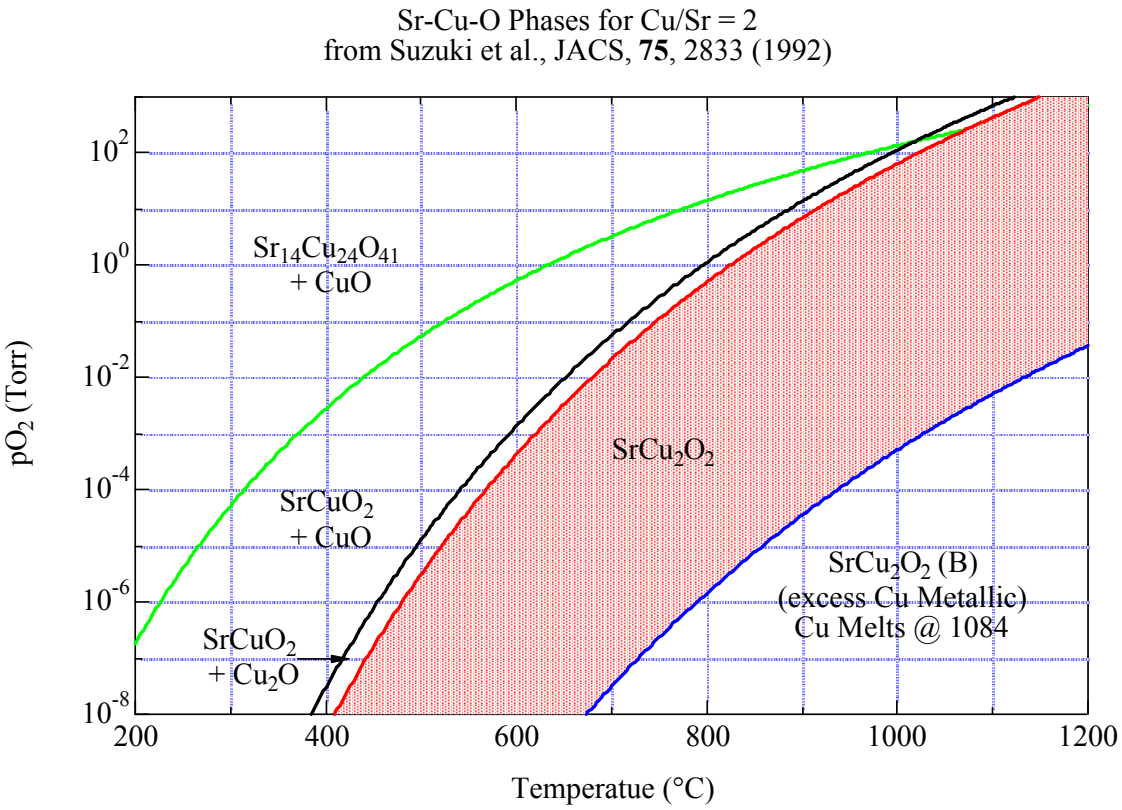
Sr-Cu-O Phases for Cu/Sr = 2
from Suzuki et al., JACS, 75, 2833 (1992)
pO2 (Torr)
10^2
10^0
10^-2
10^-4
10^-6
10^-8
200
400
600
800
1000
1200
Temperatue (°C)
Sr14Cu24O41 + CuO
SrCuO2 + CuO
SrCuO2 + Cu2O
SrCu2O2
SrCu2O2 (B)
(excess Cu Metallic)
Cu Melts @ 1084

Figure 2

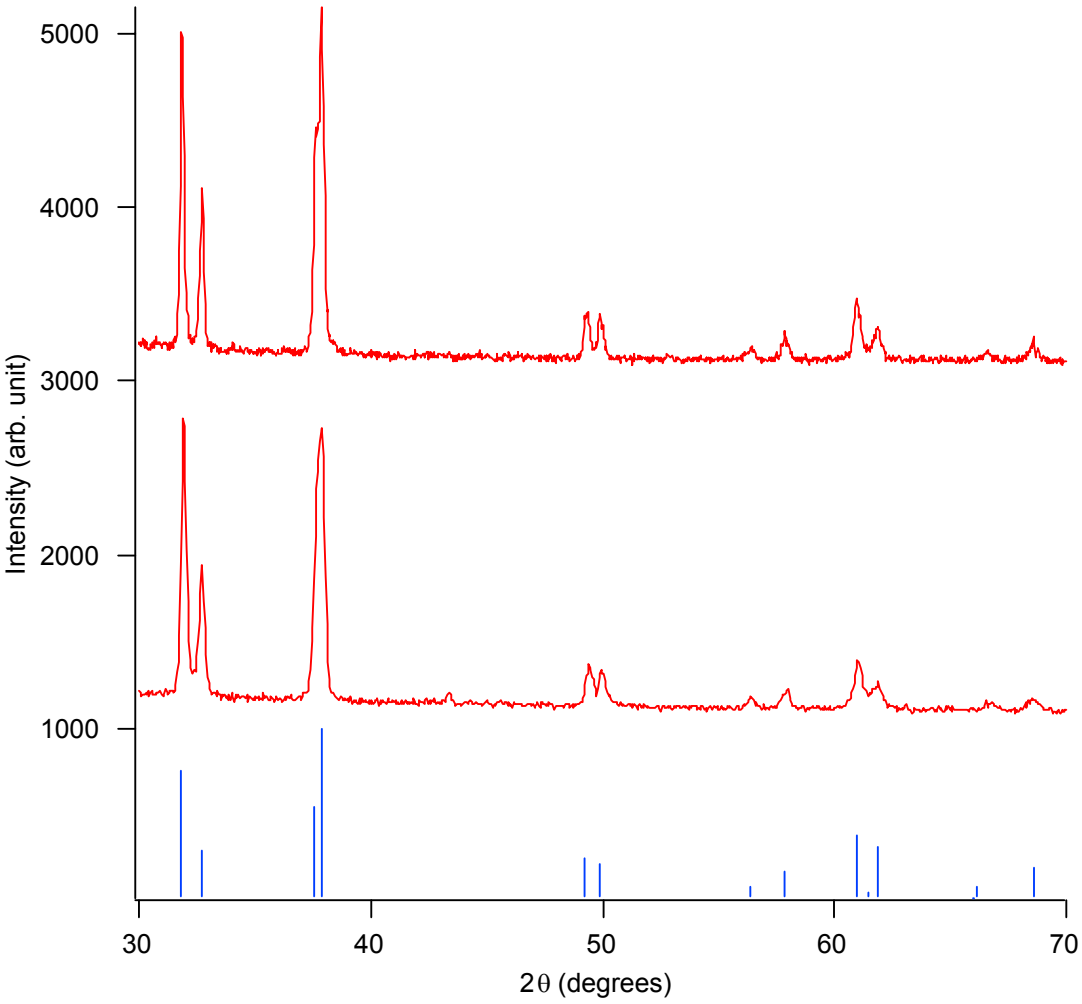
5000
4000
3000
2000
1000
Intensity (arb. unit)
30
40
50
60
70
2θ (degrees)

Figure 3

	Copper	Strontium	Calcium
$SrCu_2O_2$ precursor	1.00	0.50	0.00
$SrCu_20_2$ annealed	1.00	0.64	0.00
Ca substituted $SrCu_2O_2$ precursor	1.00	0.45	0.05
Ca substituted $SrCu_2O_2$ annealed	1.00	0.57	0.06

Table 1

	Copper	Strontium
Preanneal	1.00	0.56
Anneal	1.00	0.30
Anneal	1.00	0.26

Table 2

Frequency	500 Hz
Voltage	35 V
Rise	3.0 μs
Dwell	20.0 μs
Fall	6.0 μs
Echo	40.0 μs
Final Rise	3.0 μs

Table 3